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Thompson et al.

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[54] **BISMUTH AND COPPER BALLISTIC MODIFIERS FOR DOUBLE BASE PROPELLANTS**

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[73] Assignee: **The United States of America as represented by the Secretary of the Navy**, Washington, D.C.

[21] Appl. No.: **605,816**

[22] Filed: **Feb. 23, 1996**

[51] **Int. Cl.**[6] **C06B 45/10**; C06B 25/26

[52] **U.S. Cl.** **149/98**; 149/17.8; 149/96; 149/97

[58] **Field of Search** 149/19.8, 96, 98, 149/97

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,202,714	5/1980	Alley et al.	149/109.4
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4,420,350	12/1983	Camp et al.	179/98

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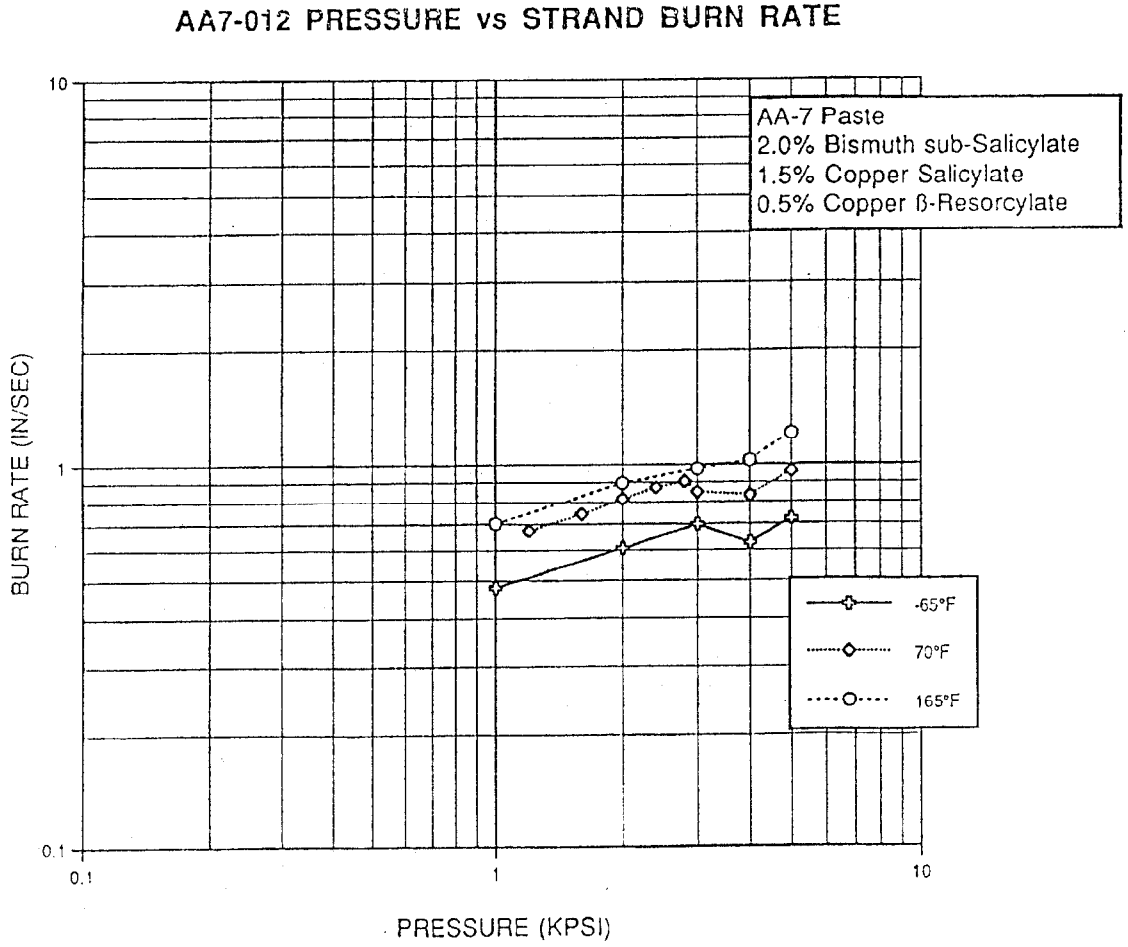
Attorney, Agent, or Firm—John Forrest; Roger D. Johnson

[57] **ABSTRACT**

Double base propellants having a mixture of bismuth and copper salts of hydroxy-substituted benzoic acids added as burning rate (ballistic) modifiers.

12 Claims, 15 Drawing Sheets



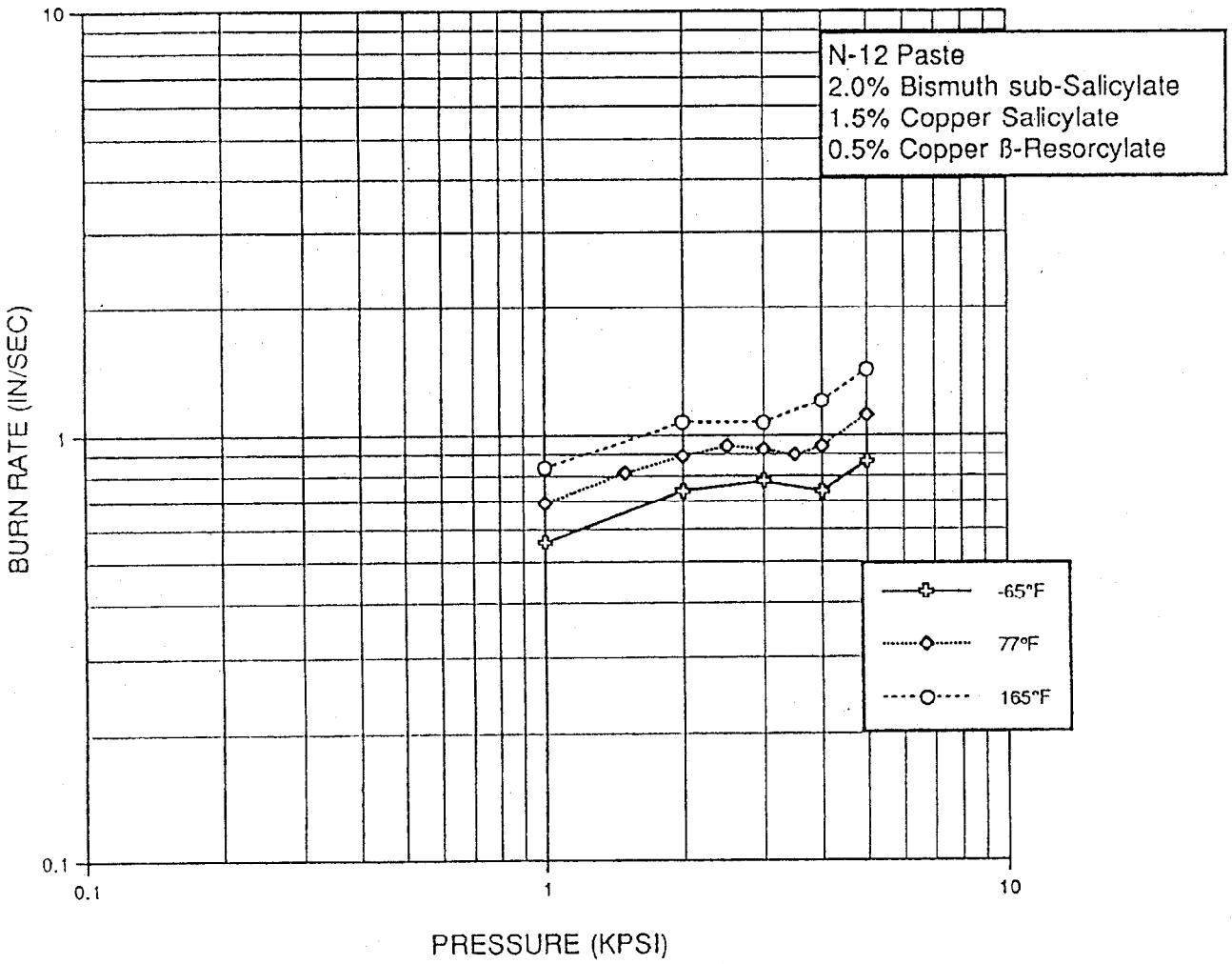

N12-041 PRESSURE vs STRAND BURN RATE
N-12 Paste
2.0% Bismuth sub-Salicylate
1.5% Copper Salicylate
0.5% Copper ß-Resorcylate
-65°F
77°F
165°F
BURN RATE (IN/SEC)
10
1
0.1
0.1
1
10
PRESSURE (KPSI)

Figure 2

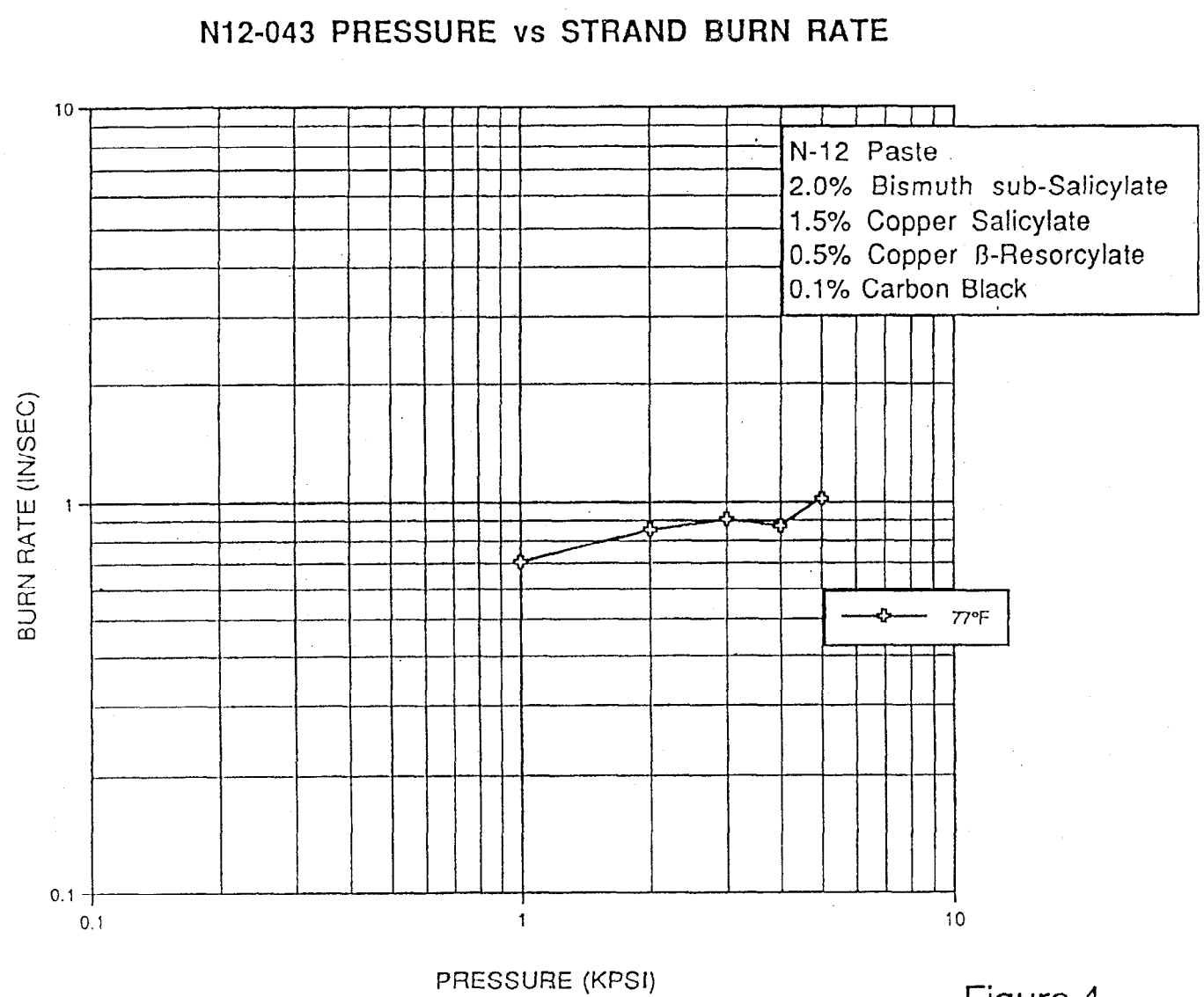

N12-043 PRESSURE vs STRAND BURN RATE
N-12 Paste
2.0% Bismuth sub-Salicylate
1.5% Copper Salicylate
0.5% Copper ß-Resorcylate
0.1% Carbon Black
77°F
BURN RATE (IN/SEC)
10
1
0.1
0.1
1
10
PRESSURE (KPSI)

Figure 4

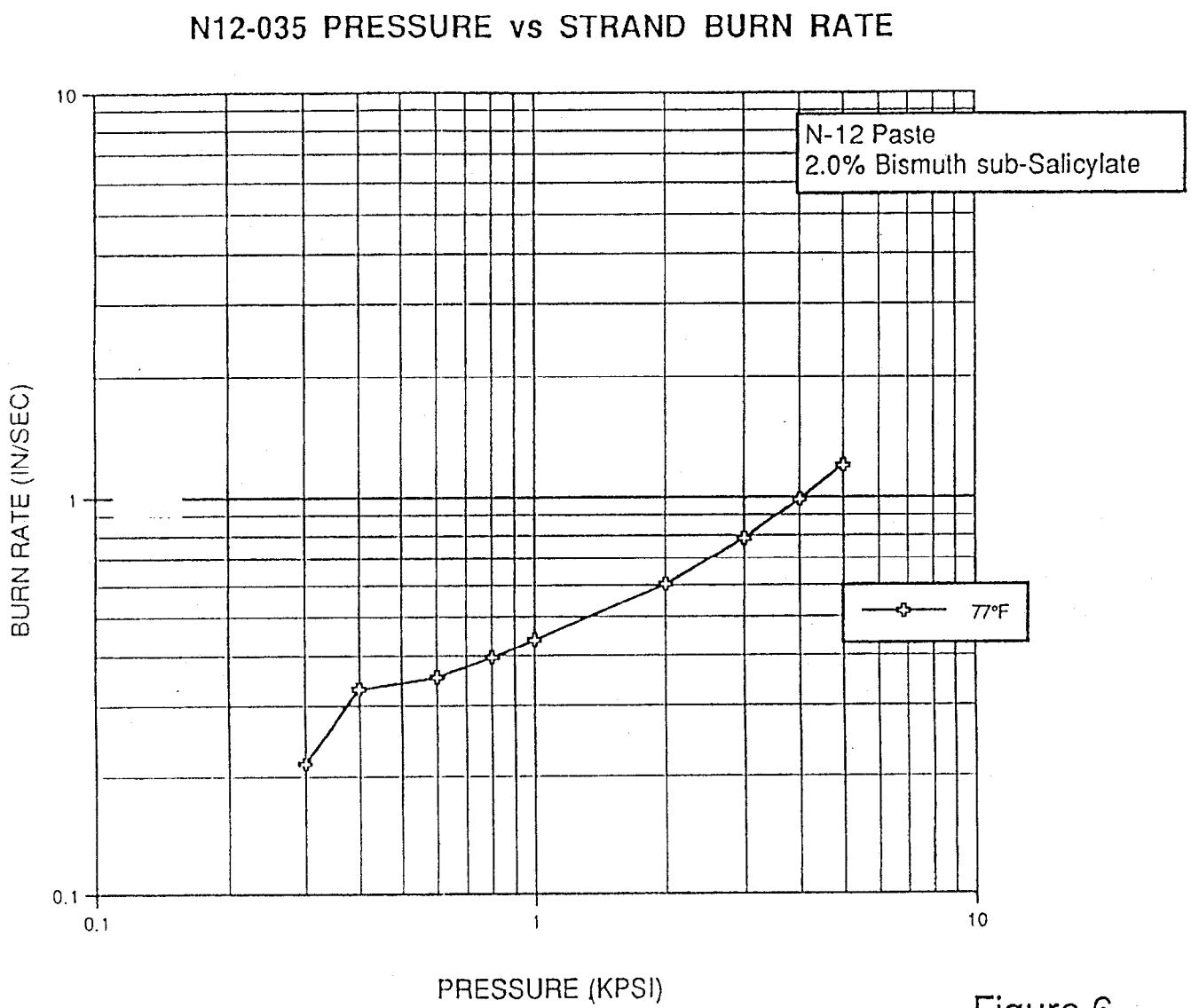

N12-035 PRESSURE vs STRAND BURN RATE
N-12 Paste
2.0% Bismuth sub-Salicylate
77°F
BURN RATE (IN/SEC)
PRESSURE (KPSI)
10
1
0.1
0.1
1
10

Figure 6

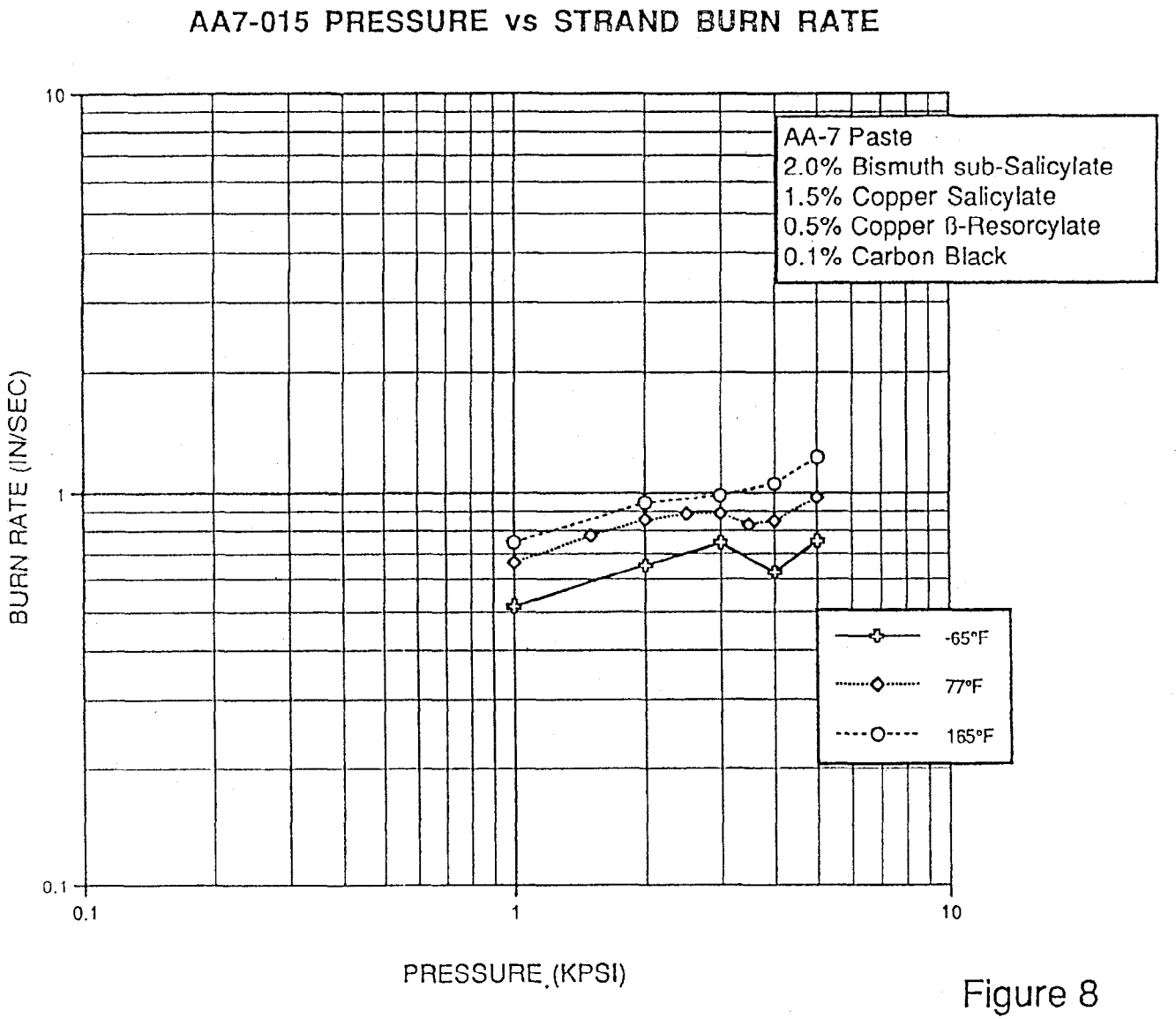

AA7-015 PRESSURE vs STRAND BURN RATE
AA-7 Paste
2.0% Bismuth sub-Salicylate
1.5% Copper Salicylate
0.5% Copper ß-Resorcylate
0.1% Carbon Black
-65°F
77°F
165°F
BURN RATE (IN/SEC)
PRESSURE (KPSI)
10
1
0.1
0.1
1
10

Figure 8

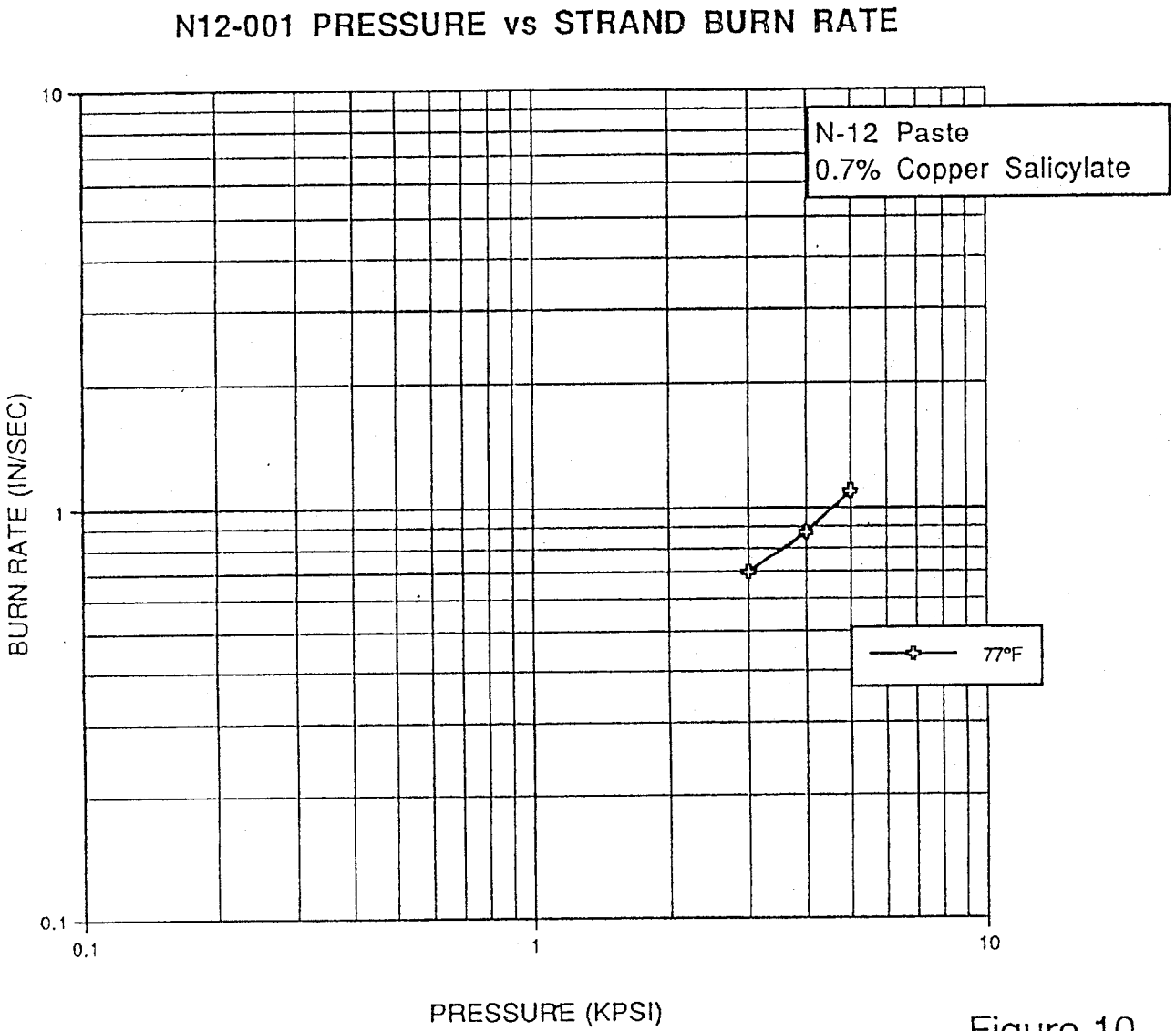

N12-001 PRESSURE vs STRAND BURN RATE
N-12 Paste
0.7% Copper Salicylate
77°F
BURN RATE (IN/SEC)
PRESSURE (KPSI)
10
1
0.1
0.1
1
10

Figure 10

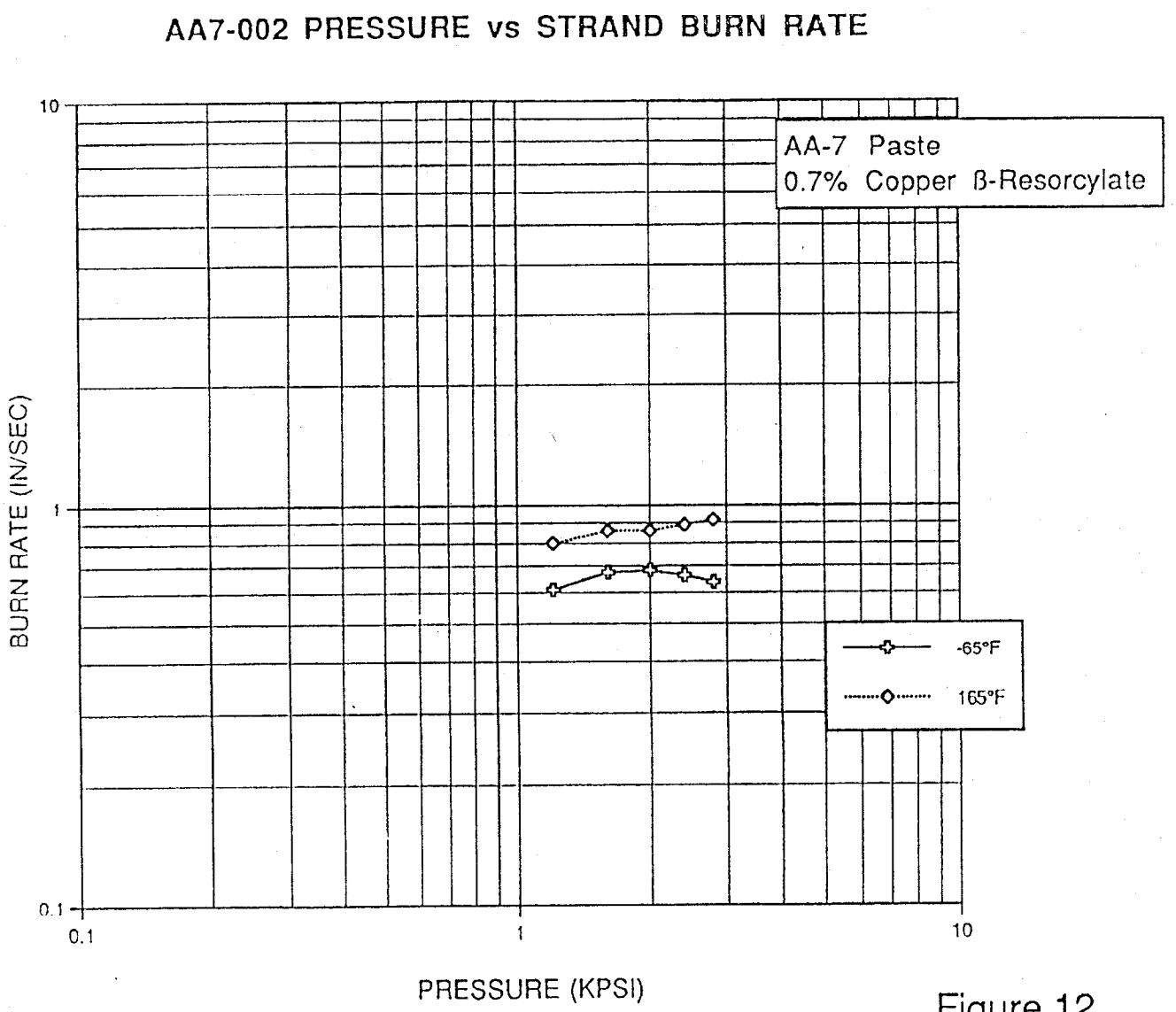

AA7-002 PRESSURE vs STRAND BURN RATE
AA-7 Paste
0.7% Copper ß-Resorcylate
-65°F
165°F
BURN RATE (IN/SEC)
PRESSURE (KPSI)
10
1
0.1
0.1
1
10

Figure 12

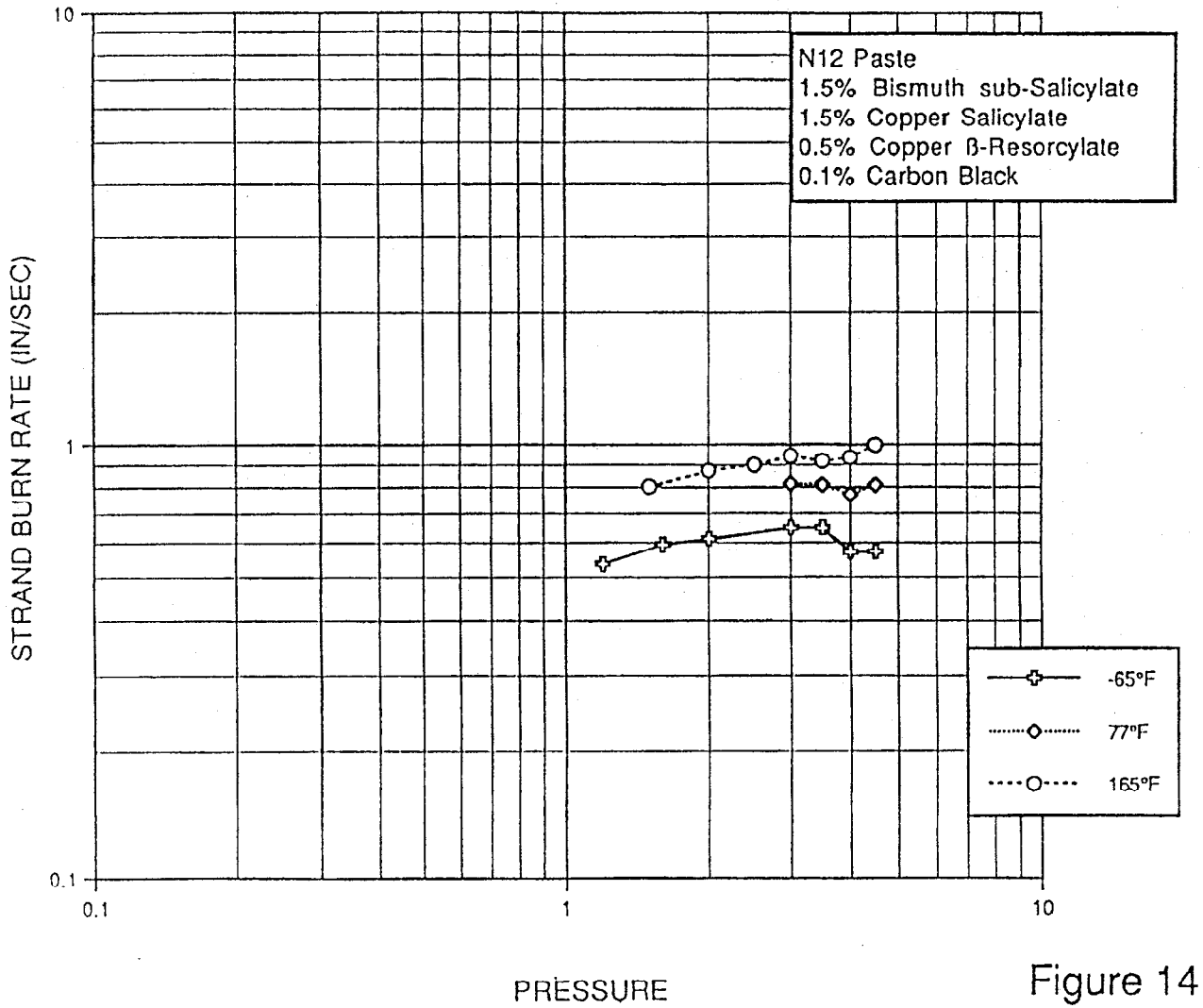

N12-055 PRESSURE vs STRAND BURN RATE
N12 Paste
1.5% Bismuth sub-Salicylate
1.5% Copper Salicylate
0.5% Copper ß-Resorcylate
0.1% Carbon Black
-65°F
77°F
165°F
STRAND BURN RATE (IN/SEC)
10
1
0.1
0.1
1
10
PRESSURE

Figure 14

BISMUTH AND COPPER BALLISTIC MODIFIERS FOR DOUBLE BASE PROPELLANTS

BACKGROUND OF THE INVENTION

The present invention relates to propellants and more particularly to burn rate modifiers for double base propellants.

A double base propellant has an energetic polymer, generally nitrocellulose, plasticized into a gel by an energetic plasticizer, generally nitroglycerine. Various additives are also included in the propellant to improve the mechanical or ballistic properties of the propellant. One such additive is termed a burn rate (or ballistic) modifier which alters the inherently high dependence of the burning rate on chamber temperature and especially chamber pressure.

The objective in burn rate modification of double base propellants is to obtain plateau or mesa burning over a desired range of pressure and burning rate level. These terms come from the shape of a log-log plot of the burn rate equation for double base propellants which is given as $r=CP^n$ or n log P+log C, wherein r is the burn rate, P is the combustion chamber pressure, C is a constant for a given propellant composition at a specific temperature, and n is a constant for on modified propellants but is a variable in modified propellants. Double base propellants with no burn rate modifiers have a constant slope, n, with a value around 0.8 to 0.9. The addition of burn rate modifiers lowers the slope and changes the burn rate over a certain range of pressure. Plateau type propellants are characterized by the pressure exponent n being less than 0.2 in certain regions of pressure. A well defined plateau would have the pressure exponent n being zero over a useful pressure range. Mesa type propellants are characterized by the pressure exponent n being less than zero in certain regions of pressure. These propellants are also relatively temperature insensitive over wider ranges of pressures. As such, it is possible to design a rocket motor or gas generator which provides steady gas output regardless of bulk temperature. Examples of such mesa type propellants are described in U.S. Pat. No. 3,138,499 by Camp, et al.

Unfortunately, the burn rate modifiers used in Camp et al ('499) must include lead salts. Double base propellant processing utilizing lead based compounds poses a hazard to the environment and to personnel in the workplace. The precursor to propellant is a water wet paste which is partially dried and plasticized into a colloidal sheet by rolling between heated calenders. It is likely that some amount of the lead compound is lost in the excess water during the rolling process and subsequently carried into the waste stream. While collection and treatment methods can help clean the wastewater and are in place for any foreign material that may enter the waste stream, the best approach is to replace the problematic compound. The lead hazards also exist for propellant scrap disposal and demilitarization of units. The use of lead salts also leads to health hazards caused by lead oxides in the exhaust gases.

What is needed is a method of producing plateau and mesa propellants without the use of lead compounds.

SUMMARY

Accordingly an object of this invention is to provide new burn rate (ballistic) modifiers for double base propellants.

Another object of this invention is to provide new burn rate modifiers that are lead-free.

Yet another object of this invention is to provide lead-free burn rate modifiers which will produce plateau and mesa burning double base propellants.

These and other objects of this invention are accomplished by providing a mixture of a bismuth salt of a hydroxy substituted benzoic acid and a copper salt or chelate of a hydroxy-substituted benzoic acid which is added to double base propellant compositions to produce plateau and mesa burning propellants.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 through 15 are graphs illustrating the pressure-burning rate relationships for various propellants tested. These graphs are discussed in the examples.

DESCRIPTION

Mixtures of bismuth and copper salts of hydroxy substituted benzoic acids are added to double base propellants as burn rate (ballistic) modifiers to produce lead-free plateau or mesa type propellants.

The bismuth acid salts preferably include normal bismuth salicylate, monobasic bismuth salicylate (bismuth subsalicylate), normal bismuth 3-hydroxybenzoate, monobasic bismuth 3-hydroxybenzoate, normal bismuth 4-hydroxybenzoate, monobasic bismuth 4-hydroxybenzoate, normal bismuth 2,4-dihydroxybenzoate (normal bismuth β-resorcylate), monobasic bismuth 2,4-dihydroxybenzoate (monobasic bismuth β-resorcylate), normal bismuth 2,5-dihydroxybenzoate, monobasic bismuth 2,5-dihydroxybenzoate, normal bismuth 2,6-dihydroxybenzoate, monobasic bismuth 2,6-dihydroxybenzoate, normal bismuth phenate, monobasic bismuth phenate, or mixtures thereof. The more preferred bismuth acid salts are normal bismuth salicylate, monobasic bismuth salicylate, normal bismuth 2,4-dihydroxybenzoate, monobasic bismuth 2,4-dihydroxybenzoate, or mixtures thereof, and still more preferred are normal bismuth salicylate, monobasic bismuth salicylate, or mixtures thereof. The monobasic bismuth acid salts are preferred over the corresponding normal bismuth acid salts. Thus, more preferred bismuth acid salts are monobasic bismuth salicylate (bismuth sub-salicylate), monobasic bismuth 3-hydroxybenzoate, monobasic bismuth 4-hydroxybenzoate, monobasic bismuth 2,4-dihydroxybenzoate (monobasic bismuth β-resorcylate), monobasic bismuth 2,5-dihydroxybenzoate, monobasic bismuth 2,6-dihydroxybenzoate, monobasic bismuth phenate, or mixtures thereof. Still more preferred bismuth acid salts are monobasic bismuth salicylate, monobasic bismuth 2,4-dihydroxybenzoate, or mixtures thereof, with monobasic bismuth salicylate being most preferred. The bismuth acid salt preferably comprises from about 0.5 to about 4, more preferably from 1.0 to 3.0, and still more preferably from 1.5 to 2.0 weight percent of the total double base propellant.

The copper acid salts preferably include normal copper salicylate, monobasic copper salicylate, normal copper 3-hydroxybenzoate, monobasic copper 3-hydroxybenzoate, normal copper 4-hydroxybenzoate, monobasic copper 4-hydroxybenzoate, normal copper 2,4-dihydroxybenzoate (normal copper β-resorcylate), monobasic copper 2,4-dihydroxybenzoate (monobasic copper β-resorcylate), normal copper 2,5-dihydroxybenzoate, monobasic copper 2,5-dihydroxybenzoate, normal copper 2,6-dihydroxybenzoate, monobasic copper 2,6-dihydroxybenzoate, copper (cupric) stannate, copper stearate, or mixtures thereof. The more preferred copper acid salts are normal copper salicylate,